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Research Article

Coprecipitation procedure for speciation of chromium in some dairy food product and water samples by FAAS

Abstract

A new method based on the coprecipitation procedure (CP) for separation/speciation using flame atomic absorption spectrometric (FAAS) determination was proposed for the determination of Cr(III)/Cr(VI) in some real samples with Co(II)/ α -Benzoin oxime precipitate. It enabled a very selective, basic and rapid method for chromium determination to be developed. The analytical variables including pH, amount of α -Benzoin oxime, amount of Co(II) as carrier element, and sample volume were investigated for the quantitative recoveries Cr(III)/Cr(VI). No interfering effects were observed from the concomitant ions when present in real samples. Cr(III) was quantitatively recovered on Co(II)/ α -Benzoin oxime precipitate at a pH range of 7–10, while Cr(VI) was not quantitatively recovered for any of the pHs. The calibration graph was linear in the range of 1.0–10.0 mg L⁻¹. Under the optimized conditions, detection limits of 0.01 μ g L⁻¹ and the relative standard deviations of 1.1% were found. The preconcentration factor was found to be 1000. The precipitate was dissolved in 0.1 mL of concentrated HNO₃, and made up to 1.0 mL with deionized ultra pure water. The validation of the presented CP was checked by the analysis of certified reference materials. The method was applied for the determination of Cr(III)/Cr(VI) in real samples such as natural waters and some dairy food samples, and good results were obtained (relative standard deviations <2%, recoveries >95%).

Introduction

Increasing industrialization and human activities have caused the emission of various pollutants into the air, soil, sediments, water and biota [1]. As a consequence of environmental pollution and the use of various fertilizers, pesticides and herbicides, contaminants may enter the food chain resulting in elevated concentrations of toxic elements and organic substances in food stuffs [2]. Once it enters the environment, its toxicity is determined to a large extent by its chemical form and species transformation [3]. Dietary factors can also influence trace element reference values in the tissues of humans [4]. Growing concern about the quality of food has initiated numerous investigations on the presence of essential and toxic trace elements in different foodstuffs [5,6]. In food analysis, extended analytical efforts have been undertaken to obtain reliable results for trace element determinations.

It is well known that the toxicological and biological properties of most elements depend on their chemical forms. Information about the oxidation state of trace elements is as important to know as its chemical structure. It has been

reported that the same metal ion may possess different levels of toxicity in its various oxidation states, which are responsible for their different physico-chemical and biological activities [7]. Speciation analysis of toxic heavy metals has special importance due to its impact on environmental chemistry, ecotoxicology, clinical toxicology and food industry.

Chromium is one of the most abundant elements on earth and it is mainly present in Cr(0), Cr(III) and Cr(VI) oxidation states, which have different toxicities, motilities and bio-availabilities. Metallic chromium is mainly found in alloys, such as stainless steel, but also in chrome-plated objects. Cr(III) which exists in natural waters in hydrolyzed Cr(H₂O)₄OH₂⁺ form and complexes, and is even adsorbed on colloidal matter. It is an essential micronutrient in the body and combines with various enzymes to transform sugar, protein and fat. Cr(III) is also used in a number of commercial products, including dyes, paint pigments and salts for leather tanning. Cr(VI) is found as CrO₄²⁻, HCrO₄⁻ or Cr₂O₇²⁻ depending on the pH of the medium. It is known to be carcinogenic and mutagenic and it induces dermatitis. It occurs in a range of compounds used in industrial processes, such as chrome plating [8–11].

Chromium is an analyte of interest to the above industries and in the environment because, like other metals, it is not biodegradable. Once it enters the environment, its toxicity is determined to a large extent by its chemical form (e.g., Cr(VI) which is much more toxic than Cr(III)) [12]. The World Health Organization (WHO) recommends a guideline value of 0.05 mg L⁻¹ for Cr in drinking water [13].

Sensitive and accurate determination of metals at trace level is one of the important aims of analytical chemistry [14]. The quantification of trace metals in food samples has routinely been conducted by inductively coupled plasma optical emission spectrometry (ICP-OES) [15], inductively coupled plasma mass spectrometry (ICP-MS) [16], and flame atomic absorption spectrometry (FAAS) [17–20]. In many cases, the analytical instrumentation available does not present the sensitivity requirements necessary to analyze chromium in food samples. Thus, several procedures have been developed for the separation and preconcentration of chromium, including liquid–liquid extraction [9], solid phase extraction [10], coprecipitation [21], and X-ray fluorescence [22].

The coprecipitation method is useful for the preconcentration of trace metal ions and is one of the most useful ways for the preconcentration/separation of trace elements from a sample matrix, and variety of coprecipitants have been studied [23–26]. This preconcentration purpose is characterized by the formation of insoluble compounds.

In the present work, we proposed a method which can be used for the determination of Cr(III) and also for the preconcentration and speciation of Cr(III/VI) species. The Co(II)– α Benzoin oxime system was proposed as a new procedure for the efficient and selective determination of Cr(III). The results presented herein summarize the most important features of the Cr(III) determination and stripping efficiencies for the CPs, as well as the selectivity of the α Benzoin oxime for Cr(III) when it appears in the presence of other metals in the aqueous phases. The Cr(III) was quantitatively separated from Cr(VI) and preconcentrated. Cr(VI) concentrations were obtained as the respective differences between total chromium and Cr(III).

To our knowledge, flame atomic absorption spectrometry (FAAS) together with the Co(II)/ α -Benzoin oxime system has not been used for the determination of Cr(III). The developed method was tested for the determination of chromium in some water samples and dairy food samples. The method can also be employed for the separation and speciation of chromium species in various natural waters.

Experimental

Instrumentation and materials

A PerkinElmer model AAnalyst 800 flame atomic absorption spectrometer (Norwalk, CT, USA) equipped with a deuterium background correction system and an air–acetylene burner was used for the determination of Cr(III) in the aqueous phase after the CP procedure. The wavelength used was 357.9 nm. A spectral bandwidth of 0.7 nm, acetylene flow rate of 1.4 L min⁻¹, and nebulizer flow rate of 10.0 mL min⁻¹ were the conventional

working parameters. A pH meter with a glass and calomel electrode pair (Nel pH 900), a magnetic stirrer (Chiltern) and an MLTW–54 model centrifuge (www.coleparmer.com) were used for centrifugation purposes.

Reagents and standard solutions

All the reagents used were of the highest available purity and at least of analytical reagent grade (Merck, Darmstadt, Germany). Deionized ultra pure water was used for the preparation of the solutions. Cr(III) and Cr(VI) stock solutions (1000 mg L⁻¹) were prepared from Cr(NO₃)₃·9H₂O and K₂CrO₄ [10]. From these solutions, dilute working solutions were prepared on a daily basis. The calibration curve was established using the standard solutions prepared in 1 mol L⁻¹ HNO₃ by dilution of the stock solutions. A 0.1% (w/v) solution of α -Benzoin oxime was prepared by dissolving 0.1 g of the reagent in 100 mL of methanol. The glassware used was cleaned by soaking overnight in dilute HNO₃ (1:5) and then rinsed with deionized water several times.

The reduction of Cr(VI) to Cr(III) was carried out using hydroxylamine hydrochloride as the reducing agent. The following buffer solutions were used for the presented preconcentration procedure: HCl/KCl buffer for pH 1.0–2.0; CH₃COONa/CH₃COOH buffer for pH 3.0–5.0; CH₃COONH₄/CH₃COOH buffer for pH 6.0–7.0 and NH₃/NH₄Cl buffer for pH 8.0–10.0.

Preparation of food samples

A 0.5-g amount of the standard reference material (INCT-TL-1 tea leaves; <http://www.ist-world.org>) was dissolved with a mixture of 10 mL of concentrated HNO₃ and 2 mL of concentrated H₂O₂ on a hot plate. After completing the dissolution process, all the sample solutions were clear. The volume of the samples was diluted to approximately 25 mL using deionized water. The final measurement volume of the sample solutions was 1 mL.

The second certified reference material was an SPS-WW2 Batch 108 waste water (<http://www.ist-world.org>) sample. The pHs of 10-mL aliquots of the samples were adjusted to 8.0 with NH₃/NH₄Cl buffer solution. Then the Co(II)/ α -Benzoin oxime CP given above was applied to these sample solutions.

First of all, 1.0-g aliquots from each of the food samples were treated with 10 mL of nitric acid and then heated until a clear solution was obtained. After this, the evaporation was continued almost to dryness, and 10 mL of nitric acid was again added to the moist residue. The mixture was evaporated to near dryness and then 2 mL of concentrated H₂O₂ was added to each food sample solution. After completing the dissolution process, the sample solution was filtered through a cellulose filter paper and then it was washed with 1–2 mL of 1 mol L⁻¹ HNO₃. The filtrate was diluted to 25 mL with deionized ultra pure water. These sample solutions were analyzed by using the procedure described above. The final measurement volume of the sample solutions was 1 mL. A blank digest was carried out in the same way.

The method was also applied to various water samples. First, the pHs of the water samples were adjusted to 8.0 with $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer solution and then the coprecipitation procedure was applied. The concentration of Cr(III) in the final measurement solution was determined by FAAS.

Recommended procedure

The CP method was tested with model solutions prior to its application to real samples. Twenty five milliliter portions of aqueous solutions containing 20 μg each of Cr(III) were placed into centrifuge tubes. The pH of the solutions was adjusted to 8.0 with $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer solution (1 mL). Then 0.25 mL of 1000 mg L^{-1} Co(II) as a carrier element and 0.1 mL of 0.1% (w/v) α -Benzoin oxime solution were added to the sample. After the formation of the precipitate, the sample solution was centrifuged at 3000 rpm for 10 min. The supernatant was removed. The precipitate which remained adhering to the bottom of the tube was dissolved with 0.1 mL of concentrated HNO_3 . Then the final volume was completed to 1 mL with deionized ultra pure water. The analytes in the final solution were determined by FAAS.

Results and Discussion

Effect of pH

Adjustment of the pH value was the first parameter considered on the speciation of Cr(III) and Cr(VI) with the Co(II)/ α -Benzoin oxime complex using the CP. Different pH buffer solutions were added to the experimental solution in the range of 1–10 for this study and then the CP was applied. The effect of pH on the recoveries of Cr(III) and Cr(VI) ions are given in figure 1. The recoveries of Cr(III) were quantitative in the pH range of 7.0–10.0, while Cr(VI) was not quantitatively recovered for any of the pHs. Therefore, subsequent experiments were performed at pH 8.0.

Effect of the amount of α -Benzoin oxime

The effects of the amount of α -Benzoin oxime on the recovery of Cr(III)/Cr(VI) ions on the CP system were also investigated at pH 8.0. Different amounts of α -Benzoin oxime were tested in the range of 0.0–400 μL of 0.1% (w/v) α -Benzoin oxime. Quantitative recovery was achieved in the range of 150–400 μL of coprecipitating reagent. The results are shown in figure 2. When the experiments were performed without α -Benzoin oxime at pH 8.0, the recovery values were not quantitative ($\leq 15\%$) for studying the metal ions. These results show that α -Benzoin oxime reagent is necessary for the quantitative recoveries of Cr(III)/Cr(VI) ions. For all the subsequent works, 250 μL of 0.1% (w/v) α -Benzoin oxime solution was used.

Effect of the amount of cobalt(II) as carrier element

The effects of the amount of Co(II) as carrier element on the recoveries of Cr(III)/Cr(VI) ions were also investigated. The recoveries were not quantitative values without Co(II). The recoveries of Cr(III) were enhanced in the range of 0.1–1.0 mg of Co(II) for the formation of Co(II)/ α -Benzoin oxime precipitate at pH 8.0. The results are shown in figure 3. In the light of these results, a 0.3 mg amount of Co(II) was selected as carrier in all subsequent works.

Effects of duration time

The effects of duration time for the Co(II)/ α -Benzoin oxime precipitate on the recoveries of Cr(III)/Cr(VI) were also studied in the time range of 5–30 min. Quantitative recoveries for Cr(III) were obtained after 5 min of duration time while Cr(VI) was not quantitatively recovered at any duration time. The further studies were performed at 5 min duration time.

Effect of the centrifugation rate and time

For this purpose, a series of experiments were conducted at different centrifugation rates varying from 1000 to 4000 rpm for 10 min at optimal conditions for Co(II)/ α -Benzoin oxime precipitate. The recoveries sharply increased up to the centrifugation rate of 2500 rpm, and then remained almost

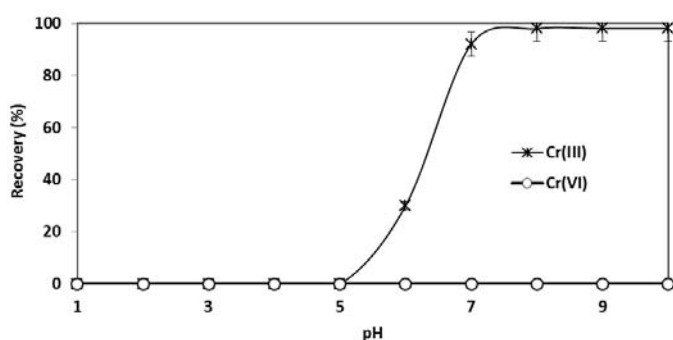


Figure 1: Effect of pH on the recoveries of Cr (III)/Cr (VI) ions (n = 3).

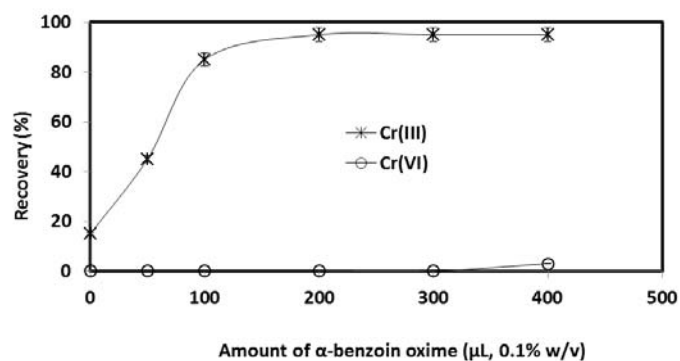


Figure 2: Effect of the amount of α -Benzoin oxime (n = 3).

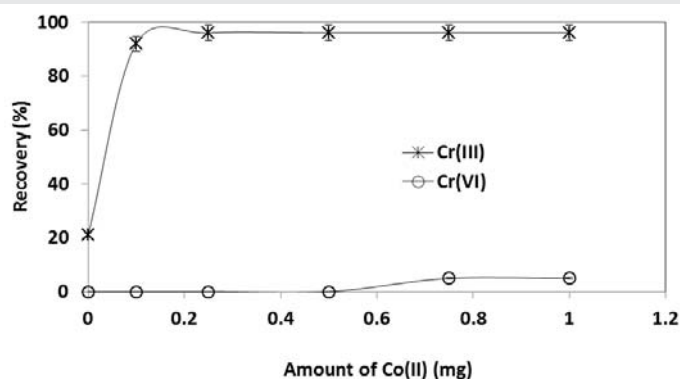


Figure 3: Effect of the amount of the Co (II) on the recovery of Cr (III)/Cr (VI) ions (n = 3).

constant. As the optimal centrifugation rate, 3000 rpm was selected (figure 4).

Another important parameter is the centrifugation time for the Co(II)/ α -Benzoin oxime CP. In order to get the best centrifugation time, the experiments were performed in the range of 5–30 min under the optimized conditions. The results showed that the centrifugation time had a significant influence on the signals of the analytes. The best results were obtained after 10 min centrifugation time. The Cr(III) signals were nearly constant beyond the centrifugation time of 10 min, as can be seen from figure 5. The optimum centrifugation time for this process was chosen as 10 min.

Sample volume and preconcentration factor

The effect of sample volume is a very important parameter for the CP. The effect of sample volume on the recoveries of Cr(III) was examined in the range of 25–1000 mL by using model solutions prepared at the optimal conditions. The results of this study are shown in figure 6. The results show that the quantitative recoveries were obtained up to 1000 mL of sample volume for Cr(III) ions except for Cr(VI). The preconcentration factor was calculated by the ratio of the highest sample volume and the lowest final volume for Cr(III). Eventually, a preconcentration factor of 1000 can be achieved when the final volume was 1.0 mL.

Determination of total chromium

In order to reduce Cr(VI) to Cr(III), various reducing

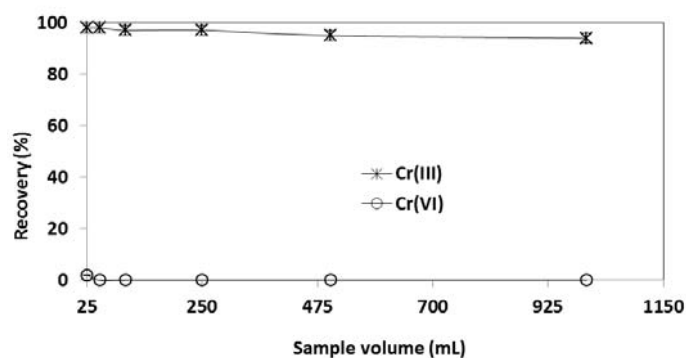


Figure 6: Effect of sample volume on the recoveries of Cr (III)/Cr (VI) ions (n = 3).

reagents were studied. The pH of a 25 mL aliquot of the test solution including 20 μ g of Cr(III) was brought to pH 1 with 2 mol L⁻¹ H₂SO₄. Then, 10-mL of reducing reagent was added to this solution, and it was heated for 30 min on a hot plate. As reducing agent, 5% (w/v) Na₂SO₃, 5% (w/v) HONH₂·HCl, 5% (w/v) KI and 5% (w/v) NaNO₂ solutions and ethanol were tested and then the described procedure was applied. The obtained recovery values were $\leq 20\%$. The quantitative recoveries were obtained by another reducing procedure as follows: to 25 mL of the test solution were added 0.25 mL of 1 mol L⁻¹ HNO₃ and 1 mL of 1% (w/v) HONH₂·HCl, respectively. The solution was allowed to stand at room temperature for 30 min [10]. After the reduction of Cr(VI) to Cr(III), the pH was adjusted to 8.0 with NH₃/NH₄Cl buffer for Co(II)/ α -Benzoin oxime precipitate and the volume was made up to 25 mL with deionized water. These results show that the recoveries of total chromium were higher than 98%.

Effect of matrix ions

To detect potential interferences on the Co(II)/ α -Benzoin oxime precipitate of Cr(III) (20 μ g), various amounts of Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻ and PO₄³⁻, and also Fe(III), Cu(II), Zn(II) and Ni(II) ions at mg L⁻¹ and/or higher levels may have interferic effects on the determinations of Cr(III) ions by flame atomic absorption spectrometry. The results are given in table 1. These results show that this Co(II)/ α -Benzoin oxime procedure could be applied successfully for the speciation of Cr(III) and Cr(VI) at pH 8.0. These potentially interfering ions did not interfere under the experimental conditions used.

Analytical performance of the method

The analytical performances of the procedure for chromium species were calculated using the results obtained from FAAS measurements. The precision of the method was found to be 1.1% as the relative standard deviation by analyzing tap water samples (n = 8). The limit of detection (LOD) of the presented coprecipitation study was calculated as 0.01 μ g L⁻¹ under optimal experimental conditions (pH: 8.0, sample volume: 1000 mL, final volume: 1 mL) by applying the developed procedure and analyzing 20 blank solutions (3s). In the calculation of the LOD of the method, the 1000-fold preconcentration factor was taken into consideration.

The equation of the calibration curve obtained after applying

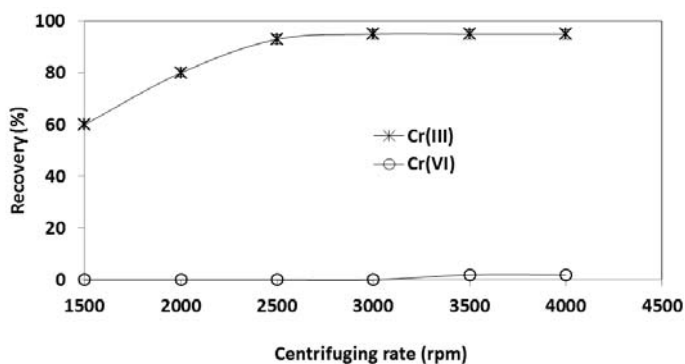


Figure 4: Effect of centrifugation rate on the recoveries of Cr (III)/Cr (VI) ions (n = 3).

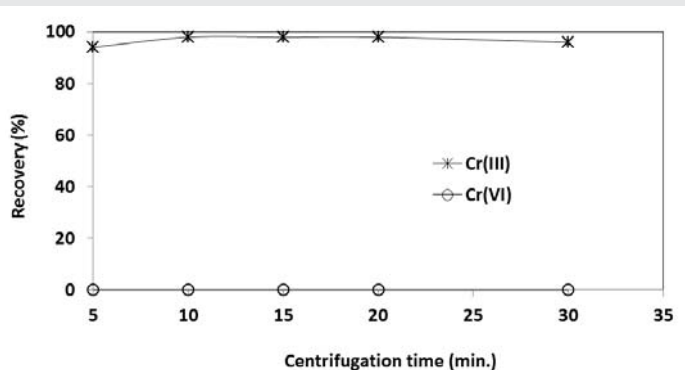


Figure 5: Effect of centrifugation time of on the recoveries of Cr (III)/Cr (VI) ions (n = 3).

the CP was $A = 0.0452C_{Cr} + 0.0005$, where A is the absorbance and C_{Cr} is the chromium(III) concentration. Linearity was observed over the range of 0.5–10 mg L⁻¹ ($r^2 = 0.998$).

Application of some real samples

The validation of the presented procedure was performed by the analysis of two certified reference materials (CRM), namely INCT-TL-1 tea leaves and SPS-WW2 Batch 108 waste water sample. The certified and observed values for certified reference materials are given in table 2. The results found were in good agreement with the certified values of CRMs. Our data showed excellent agreement with the certified values.

The recovery studies for Cr(III) ions were performed for tap water, red mullet and green tea samples. Certain amounts of the analytes were spiked to the sample solutions in order to estimate the accuracy of the presented procedure. The results are given in table 3. Good agreement was obtained between the added and found analyte contents using the recommended procedure.

The proposed method was also successfully applied for the determination of Cr(III) and total chromium in some food samples (Table 4) and water samples (tap water, mineral water, well water and waste water) (Table 5).

Conclusions

The Co(II)/ α -Benzoin oxime coprecipitative preconcentration procedure described above facilitates a selective enrichment of Cr(III) in the presence of Cr(VI) from very dilute solutions. The coprecipitation methods could be performed within about 30 min. The preconcentration factor was achieved as 1000. The achieved detection limits of the analytes are superior to some preconcentration/separation methods. The method was also free of interference compared to conventional procedures to determine the analyte metal ions. The presented coprecipitation method can be applied not only to water but also to food samples. Consequently, the procedures are fast, precise, reliable and economic.

Table 1: Influences of some foreign ions on the recoveries of Cr(III) (pH 8.0, initial sample volume: 25 mL, final sample volume: 1 mL).

Ions	Added as	Concentration (mg/L)	Recovery (%)
Na ⁺ 7	NaNO ₃	15 000	99 ± 1 ^a
K ⁺	KNO ₃	5 000	100 ± 2
Ca ²⁺	Ca(NO ₃) ₂ ·4H ₂ O	5 000	100 ± 2
Mg ²⁺	Mg(NO ₃) ₂ ·6H ₂ O	5 000	99 ± 1
Fe ³⁺	Fe(NO ₃) ₂ ·6H ₂ O	10	96 ± 2
Cu ²⁺	Cu(NO ₃) ₂ ·4H ₂ O	10	98 ± 1
Zn ²⁺	Zn(NO ₃) ₂ ·4H ₂ O	10	99 ± 2
Ni ²⁺	Ni(NO ₃) ₂ ·6H ₂ O	10	96 ± 1
SO ₄ ²⁻	Na ₂ SO ₄	5 000	101 ± 2
Cl ⁻	NaCl	12 000	98 ± 2
H ₂ PO ₄ ⁻	NaH ₂ PO ₄ ·2H ₂ O	500	98 ± 1

^a Average ± standard deviation.

Table 2: The determination of chromium in the standard reference materials (n = 3).

Element	INCT-TL-1 Tea leaves (µg/g)		SPS-WW2 Batch 108 waste water (µg/L)	
	Certified value	Found	Certified value	Found
Cr	1.91 ± 0.22 ^a	1.90 ± 0.05	1000 ± 5	996 ± 1

^a Average ± standard deviation.

Table 3: The determination of Cr(III) in various samples after the application of the CP (n = 3).

Sample	Added	Found	Recovery (%)
Tap water (mg/L)	-	-	-
	5	4.92 ± 0.05 ^a	98 ± 1
Red mullet (µg/g)	-	0.06 ± 0.01	-
	5	4.90 ± 0.14	97 ± 1
Green tea (µg/g)	-	0.46 ± 0.08	-
	5	5.31 ± 0.12	97 ± 1

^a Average ± standard deviation.

Table 4: Determination of total chromium in some dairy food samples after application of the proposed coprecipitation procedure (n = 3).

Sample	Total chromium (µg/g)
Black tea	1.02 ± 0.05 ^a
Heath leaf tea	0.51 ± 0.04
Green tea	0.38 ± 0.08
Bay leaf tea	0.58 ± 0.01
Island tea	0.94 ± 0.04
Rosemary tea	1.42 ± 0.04
Coffee	1.24 ± 0.05
Pomegranate flower tea	0.51 ± 0.08
Daisy tea	^b
Red mullet	0.08 ± 0.01
Carnation	0.59 ± 0.04
Corn	0.073 ± 0.004
Rice	0.024 ± 0.002
Garbanzo	0.43 ± 0.02
Sesame	0.28 ± 0.03
Potato	0.62 ± 0.08
Linseed	0.016 ± 0.004
Cabbage	0.088 ± 0.004
Eggplant	0.55 ± 0.09
Bean	0.99 ± 0.11
Flour	0.24 ± 0.04
Cheese	0.28 ± 0.06
Yogurt	0.25 ± 0.05
Milk	0.42 ± 0.02
Honey	1.08 ± 0.02
Wheat	0.27 ± 0.01
Egg	0.08 ± 0.01
Mussels	1.52 ± 0.09
Anchovy	0.084 ± 0.005
Trout	0.11 ± 0.01

^a Average ± standard deviation.

^b Below detection limit.

Table 5: Speciation of Cr (III) and Cr (VI) and total chromium in some natural water samples (sample volume: 250 mL, n = 3, mg L⁻¹).

Samples	Cr(III)	Cr(VI)	Total Cr
Tap water	– ^a	–	–
Mineral water	0.05 ± 0.01 ^b	–	0.04
Well water	0.24 ± 0.02	0.012 ± 0.003	0.252
Waste water	0.21 ± 0.04	– ^b	0.21

^aBelow detection limit.

^bMean ± standard deviation.

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